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博 士 論 文 概 要
Doctoral Thesis Synopsis

論 文 題 目
Thesis Theme

Surface functionalized diamond and graphene solution-gate field-effect transistors and their pH sensitivities

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pH monitoring plays a major part in medical sector, food industrial, environmental and domestic use. Over the years, the researches involving pH monitor are progressing and expanding. Nowadays, pH monitoring is electrochemically done by the reaction of electrolyte components; hydronium ions ($H3O^+$) and hydroxyl ions (OH^-) with a pH sensor electrode. There are many pH sensors were fabricated to determine the $H3O^+$ and OH^- activity in an electrolyte such as platinum-hydrogen electrodes, metal/metal oxides electrodes, organic redox electrodes, liquid and gel membrane electrodes pH sensor. The most popular pH sensor is glass pH electrode which is adopting liquid internal references for pH detection. The glass pH electrode received great attention because it has high selectivity, long term stability and pH range availability. Regardless its popularity in various field, glass pH electrode is physically large and fragile due to the basic characteristics of glass, which obviously glass pH electrode is not a portable instrumentation. In addition, pH glass electrode shows instability in alkaline and HF solutions. These drawbacks of glass pH electrode have motivated the evolution of alternative pH sensor. A demand for small, stable and accurate response pH sensor leading to the innovation of field-effect transistor (FET) based sensor. In the point of pH sensing, FET sensors are substantial because the ions activity in an electrolyte at the device channel surface could be directly translated into electronic signal which can be simply processed. FET sensors attracted much attention as biosensors or specifically as pH sensor because it delivered rapid and real time detection, portable instrumentation and relatively cheap. Moreover, the FET sensor also offer surface functionalization or modification with different types of functional groups on its channel surface to improve its sensing characteristics. Various materials have been used as bulk for the FET sensors such as silicon nanowires, graphene, and compound semiconductors are reported in published literatures.

The first FET sensor concept was introduced by P. Bergveld in 1970 called ion-sensitive FET (ISFET) to measure ions activity in an electrolyte. Later, in 1971, T. Matsuo reported utilizing ISFET with a reference electrode in the solution. The ISFET is a silicon-based device and its structure is identical to traditional metal-oxide semiconductor FET (MOSFET) except ISFET employed gate electrolyte instead of gate metal. The gate electric of the device was provided by electric double layer (EDL) that created at the solution/oxide layer interface when gate voltage was applied using an Ag/AgCl reference electrode. Thereafter, researchers around the world made numerous efforts to improve the ISFET and to develop an impeccable pH sensor. Later, in 2001, H. Kawarada and his team developed diamond ISFET without using surface insulator where semiconductor surface directly exposed to electrolyte solution. They named their devices as solution-gate FET (SGFET). In comparison to silicon-based ISFET, the SGFET exhibits low drift and small hysteresis due to stability of diamond terminated surface in an electrolyte. Fabrication of diamond SGFET device is more straightforward than the Si-ISFET device. Contrary to the Si-ISFET, diamond SGFET does not require gate insulator, which give advantage of better sensitivity. In addition, diamond possess superior properties such as wide potential window, biocompatibility and surface functionalization or modification makes it excellent material for pH sensor bulk. Apart from diamond, graphene also demonstrates outstanding properties as a SGFET substrate. Graphene capture great attention from researchers due to its biocompatibility, chemical stability, functionalization capability with large surface area and remarkable high carrier mobility. Previous studies have reported many modification surface techniques on diamond and graphene substrate for pH sensing. The most studied and discussion topic found in the literatures focused on oxygen termination on both substrates. However, the methods of oxidation presented in previous studies are found to be harsh and over-oxidized the channel surface of a SGFET. Over-oxidized channel surface of a SGFET covered by highly oriented C-O surface dipoles leading to low conductivity on diamond surface.

Accordingly, the aim of this study is to explore mild oxidation method which is controllable and suitable for SGFET channel surface oxidation to provide partially oxygen moieties on diamond and graphene surface. The oxidation method we proposed in this dissertation is mild and low defective especially to delicate graphene surface. For further improvement of pH sensing, we employ non-hazardous amine termination on the diamond channel surface SGFET by nitrogen radical (N-radical) generally used for aluminum nitride or gallium nitride (GaN) molecular beam epitaxy (MBE). The prior method of amine termination on diamond surface was dangerous to personnel health as it was done under ultraviolet in an ammonia gas for a long period. Besides that, we investigated the potential of native oxide titanium (TiO_2) encapsulation on metal pads source and drain. The TiO_2 encapsulation has enable the feasibility of miniaturization of a diamond SGFET. All of the works will be explained in details in dissertation as following chapters:

Chapter 1 gives an overview about pH background. These include the definition of pH and pH monitoring trends, which starts with color change based called litmus paper to electrochemical pH sensor such as field-effect transistor (FET) device. This chapter also will be discussed materials used in this work. This dissertation will discuss two materials; diamond and graphene substrate in details. Both substrates are excellent candidate for biosensor due to its biocompatibility, chemical stability, surface modification ability, availability and low cost. And lastly, research motivation of this work is presented at the end of the chapter.

Chapter 2 focused on surface modification or functionalization on diamond and graphene substrate. The surface conductivity of diamond substrate was obtained by undoped hydrogen termination and thin layer boron-doping in microwave plasma chemical vapor deposition (MPCVD). Both of the techniques are exhibits the p-type carrier concentration in the order of 10^{13} cm^{-2}/square. Boron doping profile and Raman spectroscopy measurement of a boron-doped diamond substrate are presented in this chapter. We also presented carboxyl termination on hydrogenated diamond surface and pristine graphene surface. The oxidation of both of the substrates via sequential anodization technique (which is one novelty of this present work) generates carboxyl termination on both of the surfaces. We confirmed that the carboxyl termination via sequential anodization was mild and low defective compare to the other methods of surface functionalization by oxidation. We show Raman spectra and cyclic voltammetry of carboxyl-terminated graphene to substantiate mild oxidation using this method. Amine termination on carboxyl-terminated diamond surface was also demonstrated to explore the surface chemistry combination of carboxyl-amine termination on the diamond surface. PH sensing of these surface modifications were tested in carmody buffer solution wide pH range (pH 2-12) and the pH mechanism on these surface functionalized diamond and graphene will be discussed in Chapter 3.

Full fabrication of boron doped diamond and graphene SGFET pH sensors are outlined in **Chapter 3**.

This chapter start with discussion of the fabrication process of SGFET using black polycrystalline boron-doped diamond and pristine monolayer graphene. The fabrication of the boron-doped diamond and graphene SGFET pH sensor is almost identical except the graphene substrate does not need to be hydrogenated before the placement of metal pads on substrate. A complete boron-doped diamond and graphene SGFET was operated in an electrolyte and a commercial Ag/AgCl reference electrode was used to supply gate voltage (V_G). Sequential anodization was used to modify the hydrogenated diamond and pristine graphene surface to carboxyl termination surface. The pH sensitivity of the modified carboxyl-termination surface was investigated in carmody buffer solution wide pH range (pH 2-12). Both of diamond and graphene carboxyl terminated surface exhibits pH sensitivity at low pH region (pH 2-7) and insensitive at high pH region (pH 8-12). The diamond SGFET channel was later modified with amine termination. The pH sensing mechanism on diamond and graphene were discussed in details in this chapter.

Chapter 4 demonstrates the miniaturization of SGFET. In this chapter, we investigate the possibility of a SGFET operated in small scale size. A key challenge to miniaturization of SGFET is passivation of metal pads source and drain which commonly used epoxy resin in previous work. We found out that epoxy resin was impractical for the miniaturization of diamond SGFET devices because the metal pad areas become thicker and bulky after the epoxy dried out. Therefore, we used native titanium oxide (TiO_2) passivation layer on source and drain metal pads as an alternative to epoxy resin. With this method, the fabrication of SGFET with smaller size are possible. We fabricated diamond SGFET with TiO_2 encapsulation device with gate length down to 1.5 μm and compare its performance with similar device with gate length of 100 μm. The shorter gate length device exhibit remarkable of improvement in term of transconductance and current density. The scaling of $gm_{,\,max}$ as a function of gate length, Lg of SGFET with TiO_2 encapsulation devices, SGFET without TiO_2 encapsulation devices and boron-doped diamond SGFET devices was presented for the first time. The enhancement of $gm_{,\,max}$ was observed when the Lg was shorter regardless the type of the SGFET devices. In this chapter, we also investigated the total electric double layer capacitance (C_{dl}) of the devices. The estimated value of C_{dl} of SGFET devices with Lg= 1.5 - 500 μm are 3-5 μF/cm^2 which is adequate for diamond FET biosensor operation and in line with the value appraised by previous studies.

Chapter 5 An epitome of the work is presented in this chapter. The major findings of the research is introduction to a new oxidation techniques on SGFET channel surface using sequential anodization method. The newly-introduced method is proven to be effective for oxidation of channel surface of a SGFET. The controlled oxidation could be used to control electron affinity related parameters on boron-doped diamond, or to control surface conductivity on un-doped hydrogenated diamond. Furthermore, it demonstrates mild effect oxidation on graphene substrate. We successfully demonstrate miniaturization of diamond SGFET by implementation of TiO_2 as metal contacts encapsulation. This finding will aid the development of miniature size diamond biosensor device.

早稲田大学　博士（工学）　学位申請　研究業績書

(List of research achievements for application of doctorate (Dr. of Engineering), Waseda University)

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種 類 別 (By Type)	題名、　発表・発行掲載誌名、　発表・発行年月、　連名者（申請者含む） (theme, journal name, date & year of publication, name of authors inc. yourself)
○ Paper	S. Falina, M. Syamsul, Y. Iyama, M. Hasegawa, Y. Koga and H. Kawarada, “Carboxyl-functionalized Graphene SGFET: pH Sensing Mechanism and Reliability of Anodization,” Diam.Relat.Mater, vol. 91, pp. 15-21 (2018).
○ Paper	Shaili Falina, Sora Kawai, Nobutaka Oi, Hayate Yamano, Taisuke Kageura, Evi Suaebah, Masafumi Inaba, Yukihiro Shintani, Mohd Syamsul and Hiroshi Kawarada, “Role of Carboxyl and Amine Termination on a Boron-doped Diamond Solution-Gate Field-Effect Transistor (SGFET) for pH sensing,” Sensors 2018, vol. 18(7), 2178.
Paper	Takuro Naramura, Masafumi Inaba, Sho Mizuno, Keisuke Igarashi, Eriko Kida, Shaili Falina, Yukihiro Shintani and Hiroshi Kawarada, “Threshold Voltage Control of Electrolyte Solution Gate Field-Effect Transistor by Electrochemical Oxidation,” Applied Physic Letters, vol.111(1),013505(2017).
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Oral Presentation	Shaili Falina, Yukihiro Shintani, and Hiroshi Kawarada,"Common Gate Boron-Doped Diamond (BDD) Solution Gate FET for pH Sensor", 2017. International Conference on Solid State Devices and Materials. Sendai, Japan. 19-22 September 2017.
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